

Fractional Exponent of the Modified Stokes-Einstein Relation in the Metallic Glass-Forming Melt Pd₄₃Cu₂₇Ni₁₀P₂₀

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Abstract. The diffusion coefficient in the metallic glass-forming systems such as Pd-Cu-Ni-P exhibits a marked deviation from the Stokes-Einstein (SE) relation in the proximity of the glass transition temperature. Such a deviation is characterized by the fractional exponent p of the modified SE expression. For the material Pd₄₃Cu₂₇Ni₁₀P₂₀, it has been reported that it takes the value $p=0.75$. In this work, it is shown that the value of p is highly correlated with the ratio E_D/E_{NB} , where E_D and E_{NB} are the activation energies for diffusion coefficient D and cooperativity N_B defined by the Bond Strength-Coordination Number Fluctuation (BSCNF) model. The present paper reports that for the metallic glass-forming melt Pd₄₃Cu₂₇Ni₁₀P₂₀, the fractional exponent p can be calculated accurately within the framework of the BSCNF model.

Introduction

The metallic glass-forming Pd-Cu-Ni-P melt [1-7] has gained great interest due to the unique properties such as superior glass-forming ability and thermal stability against crystallization [8,9]. In addition, it has been shown that for the metallic glass-forming Pd₄₃Cu₂₇Ni₁₀P₂₀ melt, the temperature dependences of the diffusion coefficient of the tracer ⁵⁷Co, $D(\text{Co57})$ and the viscosity η do not follow the Stokes-Einstein (SE) law [6], especially in the low temperature region, $T_g \leq T \leq T_c$, where T_g is the glass transition temperature and T_c is the critical temperature related to the mode-coupling theory [3, 5]. At that temperature region, a large deviation from the SE relation is observed [3-5]. Such a deviation is characterized by the fractional exponent p of the modified SE relation given by [10,11]

$$D = \frac{k_B}{6\pi r} \left(\frac{T}{\eta} \right)^p, \quad (1)$$

where k_B is the Boltzmann constant. The fractional exponent p gives the degree of deviation from the SE relation ($p < 1$). Note that in the case of $p=1$, Eq. (1) reduces to the original SE expression. r is the Stokes radius. According to ref. [6], the value of r for the ⁵⁷Co tracer in Pd₄₃Cu₂₇Ni₁₀P₂₀ is adopted to be $r=0.115$ nm, and the value of p has been estimated, $p=0.75$. Their result prompted us to study the mechanism of the transport properties of metallic glass-forming Pd₄₃Cu₂₇Ni₁₀P₂₀ melt in the light of our model of viscosity, the Bond Strength-Coordination Number Fluctuation (BSCNF) model [12].

In our previous studies [13-15], the temperature dependence of the viscosity in various kinds of bulk metallic glass-forming liquids has been investigated by using the BSCNF model. There, it has been shown that some new insights on glass-forming liquids are obtained in the light of the BSCNF model. For instance, in the framework of this model, a quantity denoted as N_B was defined [13], which gives the number of structural units that form the melt. The concept of N_B has been applied to several kinds of bulk metallic glass-forming systems, and the values of N_B were evaluated at T_g [14,

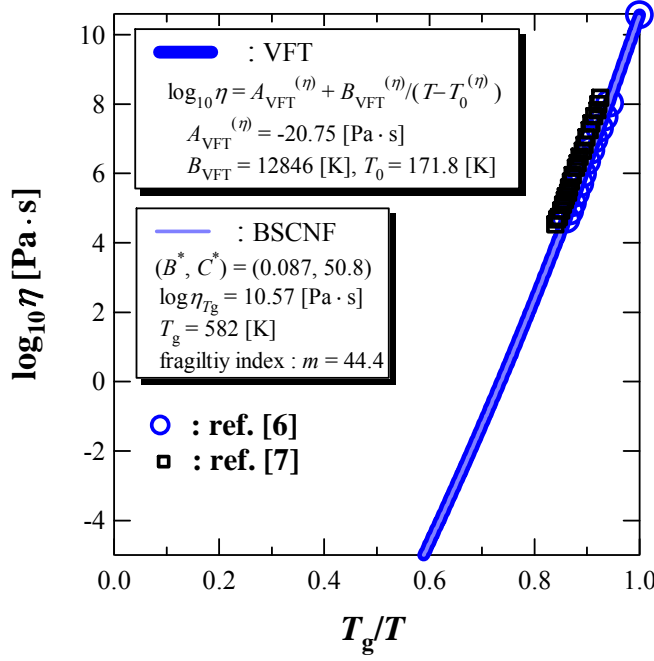


Fig. 1. Temperature dependence of the viscosity in $\text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{10}\text{P}_{20}$. The data are taken from the literature [6], where the diffusion coefficient D is calculated by using the viscosity data with the SE relation. In this figure, the high temperature data given in ref. [6] are omitted. The viscosity data measured in another work [7] is also indicated. The theoretical curves calculated by the VFT equation and the BSCNF model given in Eq. (2) are shown. The fitting parameters used in the present analysis as well as the fragility index m are given in the inset. B^* and C^* are the parameters of the BSCNF model that reproduces identically the VFT behavior [14].

Meanwhile, it has been also found that N_B can be expressed as a function of temperature [16]. Thus, N_B can quantify how the degree of cooperativity in the viscous melt changes with temperature. It should be noted that N_B is closely related to the concept of cooperatively rearranging region (CRR) proposed in the theory of Adam and Gibbs [17].

In the present work, it is shown that by relating Eq. (1) to the cooperativity described by N_B , two kinds of linear relations are obtained, that is, the relation between D and N_B , and the relation between N_B and η . The application of these relations to metallic glass-forming $\text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{10}\text{P}_{20}$ melt is also presented.

The BSCNF model and cooperativity N_B

The Bond Strength-Coordination Number Fluctuation (BSCNF) model, which was proposed by one of the authors [12], describes the temperature dependence of the viscosity of the melt in terms of the average values of the binding energy E_0 , the coordination number Z_0 , and the fluctuations ΔE and ΔZ of the structural units that form the melt. The BSCNF model is given as

$$\eta = \frac{\eta_0}{\sqrt{1 - Bx^2}} \exp \left[\frac{Cx + Cx^2 \left[\left\{ \ln \left(\frac{\eta_{T_g}}{\eta_0} \right) + \frac{1}{2} \ln(1 - B) \right\} \frac{(1 - B)}{C} - 1 \right]}{1 - Bx^2} \right], \quad (2)$$

where

$$B = \frac{(\Delta E)^2 (\Delta Z)^2}{R^2 T_g^2}, \quad \text{and} \quad C = \frac{E_0 Z_0}{RT_g}. \quad (3)$$

Here, $x = T_g/T$. η_{T_g} and η_0 are the values of the viscosity at T_g and at the high temperature limit, respectively. R is the gas constant. Details on this model have been explained elsewhere [12,13].

Fig. 1 shows the data of the temperature dependence of viscosity in $\text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{10}\text{P}_{20}$, as well as the analyses by both the Vogel-Fulcher-Tammann (VFT) equation and the BSCNF model at

temperature close to T_g . In this figure, two viscosity data taken from different works [6, 7] are shown. Note that both data differ slightly. From a theoretical point of view, it has been found that under certain condition, the behavior described by the BSCNF model becomes identical to that described by the VFT equation [14]. We can see from Fig. 1 that the behavior of the BSCNF model is identical to that of the VFT equation.

It has been pointed out that the analysis by the BSCNF model has some merits compared with that by the VFT equation, because the physical meanings of the fitting parameters B and C are clear. Furthermore, in the framework of the BSCNF model, a quantity N_B defined as $N_B = E_\eta / (E_0 Z_0)$ has been introduced, where E_η is the activation energy for the viscous flow [13]. By taking into consideration the fact that E_η is correlated with the fragility, N_B at a temperature T can be expressed as

$$N_B(x) = \frac{\ln(10)}{C} \left(\frac{d \log_{10} \eta}{d x} \right). \quad (4)$$

By using Eq. (4), the correlations between the transport coefficients and N_B have been investigated for some room-temperature ionic liquids (RTILs) [16]. There, it has been found that the activation energies for the diffusivity and N_B , which are denoted as E_D and E_{NB} , are strongly correlated. In our theory, the temperature dependence of the activation energies E_a for the transport coefficients A are calculated by using the Arrhenius equation, $A = A_0 \exp(\pm E_a / (RT))$, where A_0 is the pre-exponential factor. By relating the fractional SE relation given in Eq. (1) to N_B , the following relation is derived,

$$D \propto \left(\frac{T}{\eta} \right)^p \propto (N_B^{-1})^\zeta, \quad (5)$$

where the exponent ζ is the ratio of E_D to E_{NB} ,

$$\zeta = \frac{E_D}{E_{NB}}. \quad (6)$$

Here E_D and E_{NB} are the activation energies for diffusion coefficient D and cooperativity N_B . Our previous study has shown that for some RTILs investigated, the values of ζ were almost constant in a limited range of temperature where the experimental data are available [16]. Although the range of temperature considered in that analysis was well above T_g , the result suggested that the behavior given by N_B is highly correlated with the diffusions of cations and anions in RTILs. Therefore, N_B is expected to contain information on diffusivity of glass-forming liquids at temperature above T_g .

Application to $\text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{10}\text{P}_{20}$

Fig. 2 shows the temperature dependence of D in $\text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{10}\text{P}_{20}$. The data used in the present study are taken from the literature [6]. In this figure, the red circle (closed circle) denotes the tracer diffusion coefficient of ^{57}Co . The blue circle (open circle) is the diffusion coefficient that was calculated from the viscosity data using the SE relation, Eq. (1) for the case of $p = 1$ [6]. The diffusivity for other elements such as P, Cu, Ni, has been discussed in [5]. From Fig. 2, we can observe the critical temperature at $T_c = 710$ K [6]. The VFT equation for the diffusion coefficient written as $\log_{10} D = \log_{10} D_0 - B_{\text{VFT}} / (T - T_0)$ is used in the low temperature region. In ref. [18], it has been pointed out that for the glass-forming liquid that has T_c at the intermediate temperature region, the measured data of the transport coefficients cannot be reproduced with a single VFT equation over a wide range of temperature. Analogously, the BSCNF model does not fit the data of the material which has T_c , particularly in the higher temperature regions. In the present study, we are interested in the

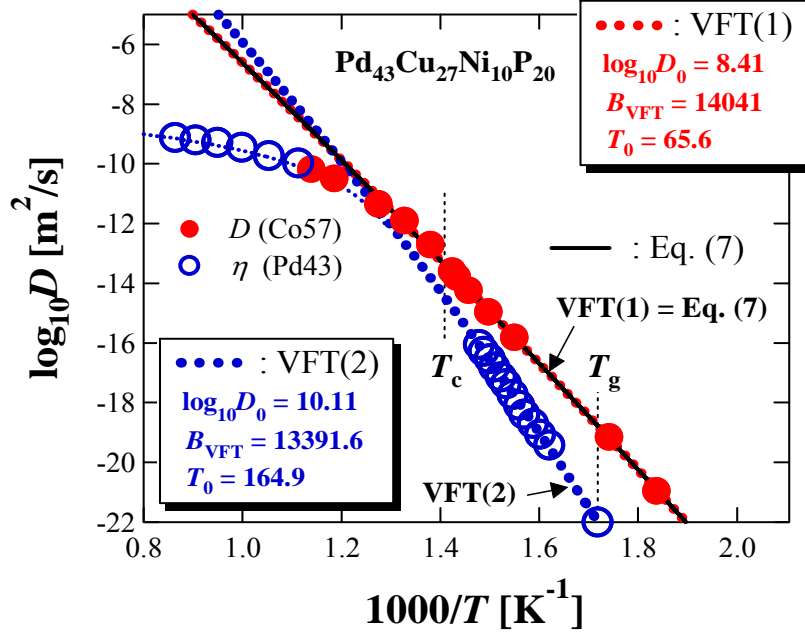


Fig. 2. Temperature dependence of the diffusion coefficient D in the metallic glass-forming melt $\text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{10}\text{P}_{20}$. The data are taken from ref. [6]. The VFT equation, $\log_{10}D = \log_{10}D_0 - B_{\text{VFT}}/(T-T_0)$, is used to fit the data of the temperature region lower than T_c . The fitting parameters of the VFT equation denoted as VFT(1) and VFT(2) are also indicated. T_c and T_g are $T_c=710$ K and $T_g=582$ K [6]. The solid line (black) is calculated by the use of Eq. (7) in such way to reproduce the curve described by VFT(1). In the analysis, $b = \log_{10}D_0$ is used.

transport mechanisms in the lower temperature region near T_g , where the activated hopping process becomes dominant. In this temperature region, various structural relaxations play important roles in the transport processes [19]. Our objective is to understand the relation between the transport properties of the melts including the viscous flow, the thermal activation and the cooperativity concomitant with the glass transition. Thus, in the present analysis, we focus on the transport properties in the temperature region $T_g \leq T < T_c$ of the metallic glass-forming melt $\text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{10}\text{P}_{20}$.

In Fig. 2, it is also shown that the VFT(1) which reproduces the data of $D(\text{Co57})$ in the low temperature region overlaps exactly the curve drawn with the solid line in black. Here, the important point is that this theoretical curve (black) is reproduced by using the following relation

$$\log_{10}D = \zeta \log_{10}(N_B^{-1}) + b, \quad (7)$$

where b is a constant. This relation is derived from Eq. (5). Note that the value of ζ is calculated from Eq. (6), and the temperature dependence of N_B is calculated from Eq. (4).

Fig. 3-(a) shows the relation between $\log_{10}D(\text{Co57})$ and $\log_{10}(N_B^{-1})$ for $\text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{10}\text{P}_{20}$, where $D(\text{Co57})$ is the diffusivity of ^{57}Co [6]. We can see from Fig. 3-(a) that the solid curve reproduced by Eq. (7) fits well the data of the low temperature region. The dashed line in Fig. 3-(a) is drawn with a simple linear function, $Y = aX + b$, with $a = 86.2$ and $b = 7.43$. We can confirm in Fig. 3-(a) that the relation given in Eq. (7) follows the linear function as well as the data.

Furthermore, Eq. (5) gives another relation between N_B and η which can be derived by relating the fractional SE relation to the BSCNF model,

$$\log_{10}(N_B^{-1}) = \left(\frac{p}{\zeta}\right) \log_{10}\left(\frac{T}{\eta}\right) + b', \quad (8)$$

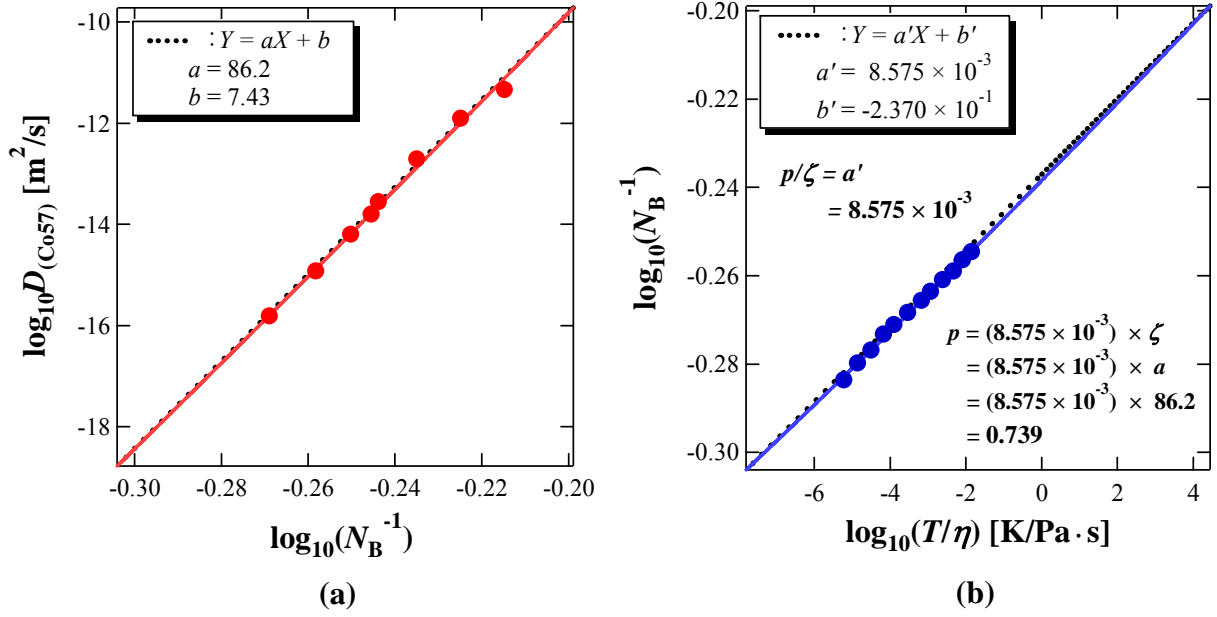


Fig. 3. (a): Relation between $\log_{10} D(\text{Co57})$ and $\log_{10}(N_B^{-1})$. Eq. (7) is described by the solid line (red). The dashed line $Y=aX+b$ is drawn simply to check the linearity of Eq. (7). (b): Relation between $\log_{10}(N_B^{-1})$ and $\log_{10}(T/\eta)$. Eq. (8) is described by the solid line (blue). Analogously to (a), the linearity of the relation is checked by comparing with $Y=a'X+b'$. The value of p in $\text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{10}\text{P}_{20}$ is computed from the value of a' with the value of a determined in figure (a).

where b' is a constant and p is the fractional exponent in Eq. (1). Eq. (8) indicates that by plotting the data of $\log_{10}(N_B^{-1})$ vs. $\log_{10}(T/\eta)$, the value of p/ζ can be determined from the slope of the linear relation as shown in Fig. 3-(b) for $\text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{10}\text{P}_{20}$. Analogously to Fig. 3-(a), an analysis with the linear function $Y=a'X+b'$ ($a' = 8.575 \times 10^{-3}$, $b' = -2.370 \times 10^{-1}$) is shown along with the viscosity data. We can confirm in Fig. 3-(b) that Eq. (8) follows almost a linear function $Y=a'X+b'$, as well as the viscosity data. From both plots shown in Fig. 3-(a) and (b), the fractional exponent p for $\text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{10}\text{P}_{20}$ can be computed. The calculated value is $p/\zeta = a' \approx 8.575 \times 10^{-3}$, where ζ is determined from Fig. 3-(a). Thus, p is calculated to be $p \approx (8.575 \times 10^{-3}) \times \zeta \approx 0.74$, which is in close agreement with $p = 0.75$ obtained from the fractional Stokes-Einstein relation.

Battezzati [19] has discussed the kinetic process of undercooled metallic melts in the proximity of glass transition temperature. There, the possibility to link the description of the breakdown of the SE relation with the mobility of atomic or molecular species at low temperature near T_g has been pointed out. On the other hand, in the present study we have shown that the rate of increase in N_B concomitant with lowering temperature is quite similar to that of $D(\text{Co57})$, the ^{57}Co tracer diffusion coefficient in the metallic glass-forming melt $\text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{10}\text{P}_{20}$. This result is expected to provide a background to understand the link between the breakdown of the SE law and the transport properties near T_g , by considering the temperature dependence of the cooperativity N_B . It is also interesting to study the relation between N_B of the bulk metallic glasses and the nature of the cluster packing [20] responsible for the structural stability.

Summary

The fractional exponent p of the modified Stokes-Einstein (SE) relation in the metallic glass-forming melt $\text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{10}\text{P}_{20}$ was discussed in the light of the Bond Strength-Coordination Number Fluctuation (BSCNF) model. In the present work, the value of p was found to be $p \approx 0.74$ which is in close agreement with the value reported by other study. The method to estimate the fractional exponent of the modified SE equation was explored in terms of the cooperativity N_B defined in the BSCNF model. The linear relations between the diffusion coefficient D and

cooperativity N_B , and between N_B and viscosity η , were derived. The result obtained in the present analysis indicates that the relations between the transport properties in glass-forming melt such as the breakdown of the SE relation can be understood in terms of the BSCNF model. A comparison of the result obtained in the present study with a possible link to the description of the fractional SE law in metallic glass-forming melts was also briefly mentioned.

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